Experimental Report

15/01/2014

Proposal: **7-05-401** **Council:** 4/2012

Title: Water dynamics in alumino-germanate nanotubes.

This proposal is continuation of: 7-01-333

Researh Area: Materials

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Samples: (OH)3Al2O3GeOH + H2O

Instrument	Req. Days	All. Days	From	To
IN4	5	4	26/06/2013	30/06/2013

Abstract:

Alumino-germanate imogolites are peculiar nanotubes having a diameter of about 2 nm and a typical length of a micron. Their strong hydrophilic character makes them extremely interesting for all applications involving transport and ultrafiltration of water, or storage of hydrogen containing materials.

In view of such potential applications, this proposals aims at investigating the diffusional and vibrational dynamics of water confined in Ge-Imo NTs, in the energy region between 0.1 and 80 meV. The IN5 spectrometer is ideally suited to study the quasielastic response (from about 0.1 to 2 meV) of liquid confined water. The IN4 spectrometer, on the other hand, is the best choice to measure the vibrational density of states (between 2 and 80 meV) in the solid phase of hydration water.

Experimental report: Dynamics of Water confined inside aluminogermanate Nanotubes

The experiment "vibrational dynamics of aluminogermanate single and double-walled nanotubes" (proposal number 7-05-401) took place at the ILL from the 5th to the 9th of December 2012.

The experimental team was composed of:
M.-S. Amara, P. Launois (LPS, Orsay)
A. Thill (LIONS, CEA Saclay)
A. Orecchini, S. Rols (ILL)

An Imogolite is a single-walled aluminosilicate nanotube having a diameter of 2 nm and a typical length of a micron. It has the empirical formula $(OH)_3Al_2O_3GeOH$ [1]. The strong hydrophilic character of imogolite nanotubes makes them extremely interesting for all applications involving transport and ultrafiltration of water, or storage of hydrogen containing materials [2].

The goal of this experiment was to measure the vibrational density of states (VDOS) of different hydrated imogolites with neutron spectroscopy. Four kinds of imogolites (all these are in form of powder) were used. The first was composed of single-walled nanotube (ISOSW-IMO) in isolated form. The second was made of isolated double-walled nanotubes(ISODW-IMO). The third contained single-walled nanotubes organized in bundle (on a 2D triangular lattice) (BUNSW-IMO). The nanotubes were hydrated prior to the experiment. From our ATG experiments, we know that desorption of water is a two steps process (see Figure 1), suggesting the presence of water having different degree of interaction with the host IMO. We refer to these two types of water to as "Confined Water" and "Bonded Water" in the following. Bulk water was also measured in the same conditions to serve as a standard. The samples were successively heated at 90°C and 250°C for 12h (off line) to vary the degree of hydration and selectively probe the different types of water. Therefore 3 spectra per wavelengths and per sample were performed:

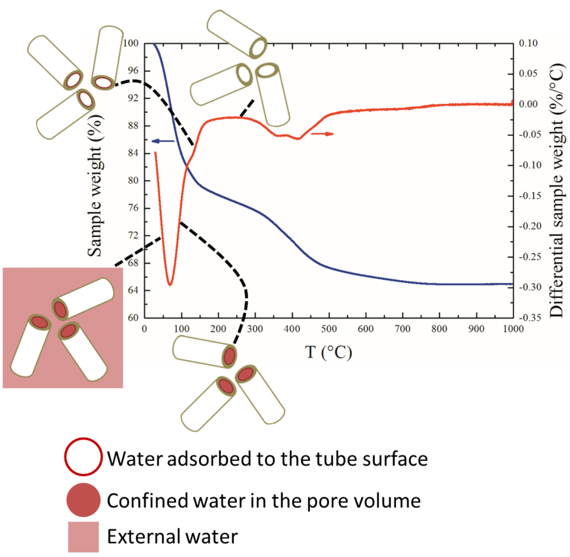

Figure 1: The ATG of hydrated ISOSW-IMO. The models for the water localization are displayed in the different temperature range.

1/ Maximum hydration = before heating
S1 = S(Bonded water) + S(confined water) + S(dry IMO)

2/ after first heating at 90°C = no confined water anymore
S2 = S(confined water) + S(dry IMO)

3/ after second heating at 250°C = no water anymore
S3 = S(dry IMO)

By performing different subtractions, the contribution of each water type can be isolated.

Two incident neutron wavelengths were used: 0.91 Å (97 meV) and 2.3 Å (14 meV). They allow probing the libration and translation modes of water respectively, with best resolution.

The results are displayed in the following figures for the ISOSW-IMO sample only. The influence of the type of tube on the spectra was found to be negligible.

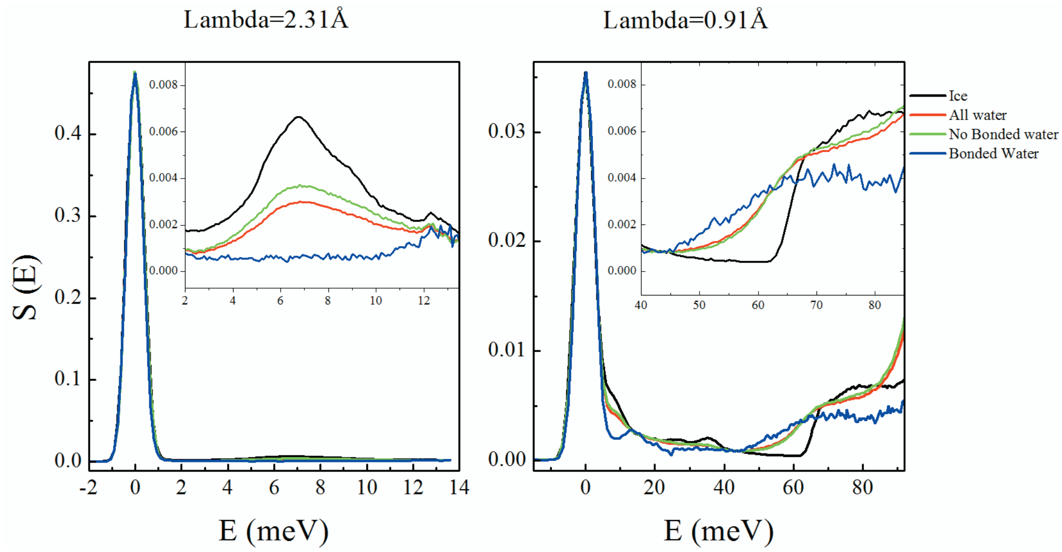

Figure 1: INS spectra measured at 2.3 Å and 0.91 Å at 10K for the ISOSW-IMO. Red =S(Bonded water) + S(confined water), Green = S(confined water), Blue = S(Bonded water), and Black = Ice Ih. The different curves were normalized to elastic intensity.

One observes that the green (confined water) and black (bulk ice) spectra share many similarities but also significant differences. Their main characteristics are located around the same typical frequencies: their first feature is located at ~ 7 meV. This peak corresponds to the optical phonons in bulk water and one can observe a fine structure, which is absent in the spectra of confined water. In addition, the integrated intensity of this peak is significantly reduced in the confined water spectrum compared to that of ice Ih. These observations might indicate an increased degree of disorder leading to an increased Debye-Waller. The libration spectrum of water (E > 40 meV) is also observed to be significantly modified under confinement with a much smoother edge at low frequency and a sharp increase in intensity at E > 80 meV.

The spectrum of bonded water (blue spectrum) present a much different aspect, especially at low frequency where the absence of lattice-like translational modes (acoustic phonon) is revealed by the disappearance of the peak at 7 meV. Librations are still observed.

In order to better understand the origin of these differences, the measures have to be extended to the high frequency range and completed by simulations.